

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 July 2008 (03.07.2008)

PCT

(10) International Publication Number
WO 2008/079807 A1

(51) International Patent Classification:

C08L 9/06 (2006.01) C08L 53/00 (2006.01)
C08L 51/06 (2006.01) B60C 1/00 (2006.01)

44303 (US). O'BRISKIE, William, J. [US/US]; 12263
Pueblo Path N.W., Uniontown, OH 44685 (US).

(21) International Application Number:

PCT/US2007/087869

(74) Agents: **HOOKER, Meredith E.** et al.; Bridgestone
Americas Holdings, Inc., 1200 Firestone Parkway, Akron,
OH 44317 (US).

(22) International Filing Date:

18 December 2007 (18.12.2007)

(81) Designated States (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH,
CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG,
ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL,
IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK,
LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW,
MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL,
PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY,
TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA,
ZM, ZW.

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

11/642,795 20 December 2006 (20.12.2006) US

(71) Applicant (*for all designated States except US*): **BRIDGE-
STONE CORPORATION** [JP/JP]; 10-1, Kyobashi
1-Chome, Chuo-ku, Tokyo, 104-8340 (JP).

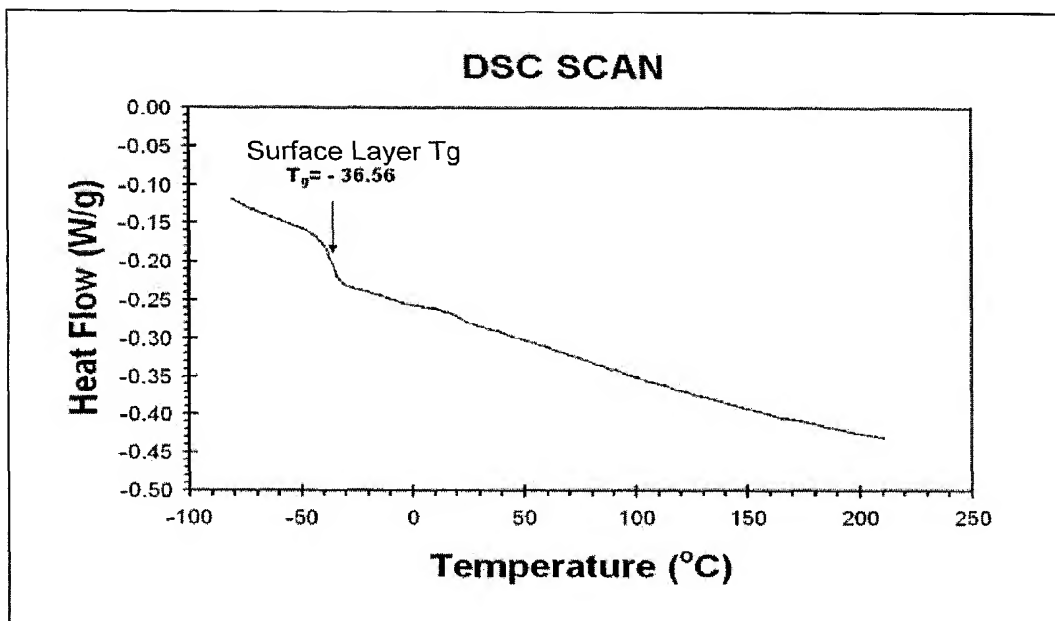
(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **KLECKNER,
James, P.** [US/US]; 154 Casterton Avenue, Akron, OH

(84) Designated States (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,

[Continued on next page]

(54) Title: RUBBER COMPOSITION CONTAINING A POLYMER NANOPARTICLE



(57) Abstract: Provided is a composition comprising at least two (mono-vinyl aromatic-conjugated diene) copolymer rubbers and a polymeric nano-particle comprising a poly (mono-vinyl aromatic) core and a poly (mono-vinyl aromatic-conjugated diene) surface layer; wherein the core of the polymeric nano-particle has a glass transition temperature (T_g) of between about 150° C and about 600° C, and the poly (mono-vinyl aromatic-conjugated diene) surface layer of the polymeric nano-particle comprises a mono-vinyl aromatic content that is between about 50 percent and about 150 percent that of the mono-vinyl content of one of the (mono-vinyl aromatic-conjugated diene) copolymer rubbers.

WO 2008/079807 A1



FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL,
PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

— *before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments*

Published:

— *with international search report*

Rubber Composition Containing a Polymer Nanoparticle

FIELD OF DISCLOSURE

[0001] The disclosure provides a rubber composition incorporating nanoparticles comprising a core and a surface layer, wherein the surface layer comprises a poly(mono-vinyl aromatic-conjugated diene) and the core has a glass transition temperature (T_g) between about 150° C and about 600° C.

BACKGROUND

[0002] On occasion, there is an increasing interest to provide tires with a high level of handling, i.e. steering response, a high level of grip, and low fuel consumption. A common method of increasing the steering response of the tire is to use a tread rubber with high stiffness. High stiffness compounds typically have a high dynamic storage modulus. Conventional compounding techniques used to increase the dynamic storage modulus include using a high filler loading, using a filler with a high surface area, using less softener, and using styrene-butadiene polymers with a high styrene content. However, each of these conventional methods has performance tradeoffs.

[0003] For example, the above mentioned conventional techniques can increase the hysteresis of the rubber compound. Increasing the hysteresis of the rubber results in more energy lost as heat, and thus increases fuel consumption.

[0004] In addition, increasing the filler loading, using a filler with a high surface area, and lowering the softener level can have a negative effect on processing, as they all increase the time it takes to disperse the filler into the rubber.

[0005] Therefore, a need remains to improve the dynamic modulus of a rubber compound without significantly impacting compound hysteresis or compound processing.

SUMMARY OF THE INVENTION

[0006] Provided is a composition comprising a rubber and a polymer nanoparticle comprising a poly(mono-vinyl aromatic) core and a poly(mono-vinyl

aromatic-conjugated diene) surface layer, wherein the core of the polymeric nano-particle has a glass transition temperature (T_g) of between about 150° C and about 600° C.

[0007] Also provided is a composition comprising at least two (mono-vinyl aromatic-conjugated diene) copolymer rubbers and a polymeric nano-particle comprising a poly(mono-vinyl aromatic) core and a poly(mono-vinyl aromatic-conjugated diene) surface layer; wherein the core of the polymeric nano-particle has a glass transition temperature (T_g) of between about 150° C and about 600° C, and the poly(mono-vinyl aromatic-conjugated diene) surface layer of the polymeric nano-particle comprises a mono-vinyl aromatic content that is between about 50 percent and about 150 percent that of the mono-vinyl content of one of the (mono-vinyl aromatic-conjugated diene) copolymer rubbers.

[0008] Additionally, a tire comprising a tread is provided. The tread comprises a rubber and a polymer nano-particle comprising a poly(mono-vinyl aromatic) core and a poly(mono-vinyl aromatic-conjugated diene) surface layer, wherein the core of the polymeric nano-particle has a glass transition temperature (T_g) of between about 150° C and about 600° C.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a graphical depiction of Differential Scanning Calorimetry analysis of the nano-particles utilized in example 1.

DETAILED DESCRIPTION

[0009] Polymer nanoparticles with a surface layer and a core with a T_g between about 150° C and about 600° C may be prepared by:

- (i) in a liquid hydrocarbon medium, polymerizing conjugated diene monomers to produce a poly(conjugated diene) block; and
- (ii) copolymerizing the poly(conjugated diene) block with a mixture of mono-vinyl aromatic monomers and multiple-vinyl aromatic monomers to produce an aromatic block.

[0010] Prior patents and publications such as U.S. patent 6,437,050 (Bridgestone Corp.) and Macromol. Symp. 118, 143-148 (1997) are incorporated herein as general references.

[0011] While step (ii) takes place, a sufficient amount of the copolymers comprising the poly(conjugated diene) block and the aromatic block may assemble to form micelle structures, and typically in the meanwhile, the aromatic blocks may be crosslinked by the multiple-vinyl aromatic monomers.

[0012] The polymer nanoparticles with a surface layer and a core with a T_g between about 150° C and about 600° C are formed through dispersion polymerization, although emulsion polymerization may also be contemplated. The polymerization may be accomplished by a multi-stage anionic polymerization. Multi-stage anionic polymerizations have been conducted to prepare block-copolymers, for example in U.S. Pat. No. 4,386,125, which is incorporated herein by reference. Other relevant references include U.S. Pat. No. 6,437,050 and U.S. Patent Application 2004/0143064.

[0013] The polymer nanoparticles can be formed from di-block copolymer chains comprising the poly(conjugated diene) block and the aromatic block. The aromatic blocks are typically crosslinked due to the presence of multiple-vinyl aromatic monomers, at least partially giving a way of controlling the core T_g . The polymer nanoparticles preferably retain their discrete nature with little or no polymerization between each other. In preferred embodiments, the nanoparticles are substantially monodisperse and uniform in shape.

[0014] The liquid hydrocarbon medium functions as the dispersion solvent, and may be selected from any suitable aliphatic hydrocarbons, alicyclic hydrocarbons, or mixtures thereof, with a proviso that it exists in liquid state during the nanoparticles' formation procedure. Exemplary aliphatic hydrocarbons include, but are not limited to, pentane, isopentane, 2,2 dimethyl-butane, hexane, heptane, octane, nonane, decane, and the like. Exemplary alicyclic hydrocarbons include, but are not limited to, cyclopentane, methyl cyclopentane, cyclohexane, methyl cyclopentane, cycloheptane, cyclooctane, cyclononane, cyclodecane, and the like. Generally, aromatic hydrocarbons and polar solvents are not preferred as the liquid

medium. In exemplified embodiments, the liquid hydrocarbon medium comprises hexane.

[0015] Any suitable conjugated diene or mixture thereof may be used as the monomer(s) to produce the poly(conjugated diene) block. Specific examples of the conjugated diene monomers include, but are not limited to, 1,3-butadiene, isoprene (2-methyl-1,3-butadiene), *cis*- and *trans*-piperylene (1,3-pentadiene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, *cis*- and *trans*-1,3-hexadiene, *cis*- and *trans*-2-methyl-1,3-pentadiene, *cis*- and *trans*-3-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, and the like, and the mixture thereof. In preferred embodiments, isoprene or 1,3-butadiene or mixture thereof is used as the conjugated diene monomer.

[0016] The polymerizing of conjugated diene monomers into a poly(conjugated diene) block is initiated via addition of anionic initiators that are known in the art. For example, the anionic initiator can be selected from any known organolithium compounds. Suitable organolithium compounds are represented by the formula as shown below:



wherein R is a hydrocarbyl group having 1 to x valence(s). R generally contains 1 to 20, preferably 2-8, carbon atoms per R group, and x is an integer of 1-4. Typically, x is 1, and the R group includes aliphatic radicals and cycloaliphatic radicals, such as alkyl, cycloalkyl, cycloalkylalkyl, alkylcycloalkyl, alkenyl, as well as aryl and alkylaryl radicals.

[0017] Specific examples of R groups include, but are not limited to, alkyls such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, n-amyl, isoamyl, n-hexyl, n-octyl, n-decyl, and the like; cycloalkyls and alkylcycloalkyl such as cyclopentyl, cyclohexyl, 2,2,1-bicycloheptyl, methylcyclopentyl, dimethylcyclopentyl, ethylcyclopentyl, methylcyclohexyl, dimethylcyclohexyl, ethylcyclohexyl, isopropylcyclohexyl, 4-butylcyclohexyl, and the like; cycloalkylalkyls such as cyclopentyl-methyl, cyclohexyl-ethyl, cyclopentyl-ethyl, methyl-cyclopentylethyl, 4-cyclohexylbutyl, and the like; alkenyls such as vinyl, propenyl, and the like;

arylalkyls such as 4-phenylbutyl; aryls and alkylaryls such as phenyl, naphthyl, 4-butylphenyl, p-tolyl, and the like.

[0018] Other lithium initiators include, but are not limited to, 1,4-dilithiobutane, 1,5-dilithiopentane, 1,10-dilithiododecane, 1,20-dilithioeicosane, 1,4-dilithiobenzene, 1,4-dilithionaphthalene, 1,10-dilithioanthracene, 1,2-dilithio-1,2-diphenylethane, 1,3,5-trilithiopentane, 1,5,15-trilithioeicosane, 1,3,5-trilithiocyclohexane, 1,3,5,8-tetralithiododecane, 1,5,10,20-tetralithioeicosane, 1,2,4,6-tetralithiocyclohexane, 4,4'-dilithiobiphenyl, and the like. Preferred lithium initiators include n-butyllithium, sec-butyllithium, tert-butyllithium, 1,4-dilithiobutane, and mixtures thereof.

[0019] Other lithium initiators which can be employed are lithium dialkyl amines, lithium dialkyl phosphines, lithium alkyl aryl phosphines and lithium diaryl phosphines. Functionalized lithium initiators may also be utilized. Preferred functional groups include amines, formyl, carboxylic acids, alcohol, tin, silicon, silyl ether and mixtures thereof.

[0020] In certain embodiments, n-butyllithium, sec-butyllithium, tert-butyllithium, or mixture thereof are used to initiate the polymerization of the conjugated diene monomers into a poly(conjugated diene) block.

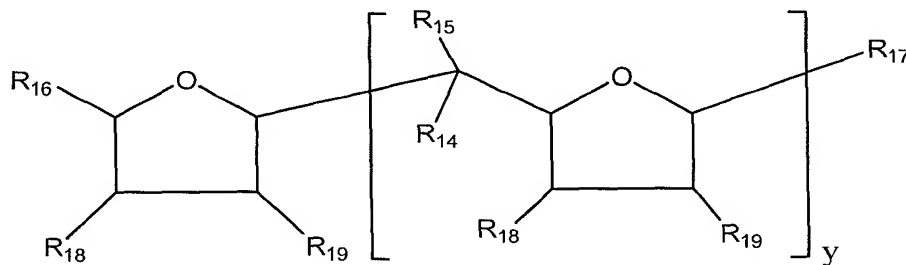
[0021] The polymerization of conjugated diene monomers into a poly(conjugated diene) block may last as long as necessary until the desired monomer conversion, degree of polymerization (DP), and block molecular weight are obtained. The polymerization reaction of this step may last from about 0.25 hours to about 10 hours, or from about 0.5 hours to about 4 hours, or from about 0.5 hours to about 2 hours. The polymerization reaction of this step may be conducted at a temperature of from about 70°F to about 350°F, or from about 74°F to about 250°F, or from about 80°F to about 200°F. In exemplified embodiments, the polymerization lasts about 90 minutes at 65-195°F.

[0022] The anionic polymerization of conjugated diene monomers may be conducted in the presence of a modifier or a 1,2-microstructure controlling agent, so as to, for example, increase the reaction rate, equalize the reactivity ratio of monomers, and/or control the 1,2-microstructure in the conjugated diene monomers. Suitable modifiers include, but are not limited to, triethylamine, tri-n-

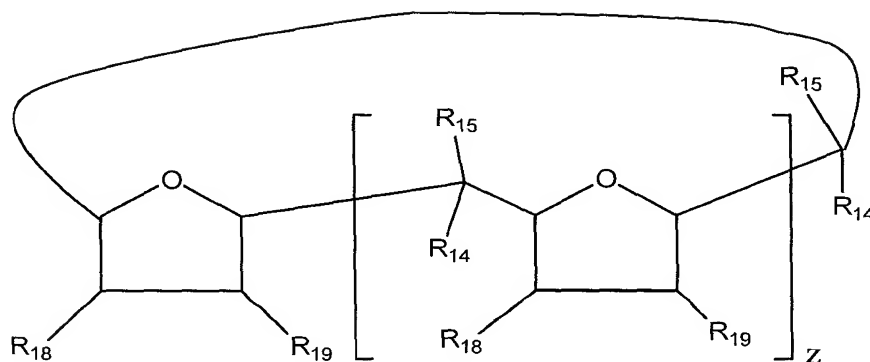
butylamine, hexamethylphosphoric acid triamide, N, N, N', N'-tetramethylethylene diamine, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether, tetrahydrofuran, 1,4-diazabicyclo [2.2.2] octane, diethyl ether, tri-n-butylphosphine, p-dioxane, 1,2 dimethoxy ethane, dimethyl ether, methyl ethyl ether, ethyl propyl ether, di-n-propyl ether, di-n-octyl ether, anisole, dibenzyl ether, diphenyl ether, dimethylethylamine, bix-oxalanyl propane, tri-n-propyl amine, trimethyl amine, triethyl amine, N,N-dimethyl aniline, N-ethylpiperidine, N-methyl-N-ethyl aniline, N-methylmorpholine, tetramethylenediamine, oligomeric oxolanyl propanes (OOPs), 2,2-bis-(4-methyl dioxane), bistetrahydrofuryl propane, and the like.

[0023] The anionic polymerization can also be conducted in the presence of an amine compound such as triethyl amine, trimethyl amine, tripropyl amine, tri-isopropyl amine, tri-n-butyl amine, and the like, and the mixture thereof.

[0024] Other modifiers or 1,2-microstructure controlling agents may be linear oxolanyl oligomers represented by the structural formula (IV) and cyclic oligomers represented by the structural formula (V), as shown below:



Formula (IV)



Formula (V)

wherein R_{14} and R_{15} are independently hydrogen or a C_1 - C_8 alkyl group; R_{16} , R_{17} , R_{18} , and R_{19} are independently hydrogen or a C_1 - C_6 alkyl group; y is an integer of 1 to 5 inclusive, and z is an integer of 3 to 5 inclusive.

[0025] Specific examples of modifiers or 1,2-microstructure controlling agents include, but are not limited to, oligomeric oxolanyl propanes (OOPs); 2,2-bis-(4-methyl dioxane); bis(2-oxolanyl) methane; 1,1-bis(2-oxolanyl) ethane; bistetrahydrofuryl propane; 2,2-bis(2-oxolanyl) propane; 2,2-bis(5-methyl-2-oxolanyl) propane; 2,2-bis-(3,4,5-trimethyl-2-oxolanyl) propane; 2,5-bis(2-oxolanyl-2-propyl) oxolane; octamethylperhydrocyclotetrafurfurylene (cyclic tetramer); 2,2-bis(2-oxolanyl) butane; and the like. A mixture of two or more modifiers or 1,2-microstructure controlling agents also can be used.

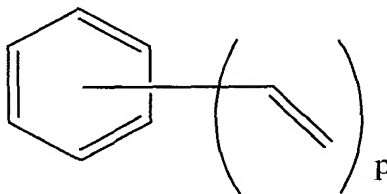
[0026] Optionally, the poly(conjugated diene) block has a randomized structure comprising conjugated diene monomers and mono-vinyl aromatic monomers that are copolymerized using an anionic initiator, optionally in the presence of a modifier. Suitable mono-vinyl aromatic monomers include, but are not limited to, styrene, ethylvinylbenzene, α -methyl-styrene, 1-vinyl naphthalene, 2-vinyl naphthalene, vinyl toluene, methoxystyrene, t-butoxystyrene, and the like; as well as alkyl, cycloalkyl, aryl, alkaryl, and aralkyl derivatives thereof, in which the total number of carbon atoms in the monomer is generally not greater than about 18; and mixtures thereof. In exemplified embodiments, the mono-vinyl aromatic monomer comprises styrene or ethylvinylbenzene or mixture thereof. If the poly(conjugated diene) block has a randomized structure comprising conjugated

diene monomers and mono-vinyl aromatic monomers, the resulting polymer nanoparticle will have a surface layer, having a copolymer comprising conjugated diene units and mono-vinyl aromatic units.

[0027] A mixture of mono-vinyl aromatic monomers and multiple-vinyl aromatic monomers may then be copolymerized with the living poly(conjugated diene) block. The weight ratio between the mono-vinyl aromatic monomers and multiple-vinyl aromatic monomers may broadly range from about 99.9:0.01 to about 0.01:99.9, preferably from about 99:1 to about 1:99, and more preferably from about 90:10 to about 10:99.

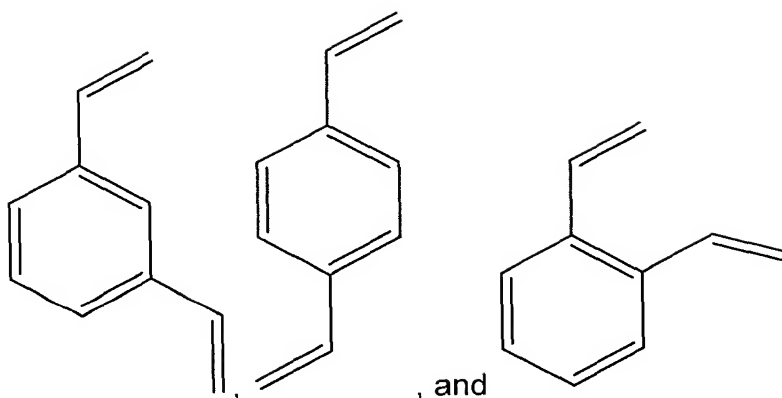
[0028] Any compound that comprises one vinyl group and an aromatic group may be used as the mono-vinyl aromatic monomer. Suitable mono-vinyl aromatic monomers include, but are not limited to styrene, ethylvinylbenzene, α -methylstyrene, 1-vinyl naphthalene, 2-vinyl naphthalene, vinyl toluene, methoxystyrene, t-butoxystyrene, and the like; as well as alkyl, cycloalkyl, aryl, alkaryl, and aralkyl derivatives thereof, in which the total number of carbon atoms in the monomer is generally not greater than about 18; and mixtures thereof. In exemplified embodiments, the mono-vinyl aromatic monomer comprises styrene or ethylvinylbenzene or mixture thereof.

[0029] Any compound that comprises two or more vinyl groups and an aromatic group may be used as the multiple-vinyl aromatic monomer. Suitable multiple-vinyl aromatic monomers include, but are not limited to compounds with a general formula as shown below:



in which p is an integer and $2 \leq p \leq 6$, preferably, p is 2 or 3, more preferably p is 2, i.e. di-vinyl-benzene (DVB).

[0030] In one embodiment, the DVB may be selected from any one of the following isomers or any combination thereof:



[0031] Additional anionic initiator such as lithium initiator may be added when the mixture of mono-vinyl aromatic monomers and multiple-vinyl aromatic monomers is copolymerized with the living poly(conjugated diene) block. Exemplary anionic initiators may be those described above. In preferred embodiments, *n*-butyllithium, *sec*-butyllithium, *tert*-butyllithium, or mixture thereof are used. The polymerization may last as long as necessary until the desired core T_g, monomer conversion, degree of polymerization (DP), and block molecular weight are obtained. The polymerization reaction of this step may last from about 0.5 hours to about 10 hours, or from about 1 hour to about 6 hours, or from about 1 hour to about 4 hours. The polymerization reaction of this step may be conducted at a temperature of from about 70°F to about 350°F, or from about 74°F to about 250°F, or from about 80°F to about 200°F. In exemplified embodiments, the polymerization step lasts 3 hours at 165°F and then 1 hour at 210°F.

[0032] It should be understood that, due to a mixture of mono-vinyl aromatic monomers and multiple-vinyl aromatic monomers being used, micelle assembly and crosslinking of the aromatic blocks may take place simultaneously.

[0033] The polymer nanoparticles are formed from the micelle-like structures with a core made from the aromatic blocks, and a surface layer made from the poly(conjugated diene) blocks.

[0034] The polymerization reactions used to prepare the polymer nanoparticles may be terminated with a terminating agent. Suitable terminating agents include, but are not limited to, alcohols such as methanol, ethanol, propanol, and isopropanol; amines, MeSiCl₃, Me₂SiCl₂, Me₃SiCl, SnCl₄, MeSnCl₃, Me₂SnCl₂,

Me₃SnCl, and etc. In exemplified embodiments, the polymerization reaction mixture was cooled down and dropped in an isopropanol/acetone solution optionally containing an antioxidant such as butylated hydroxytoluene (BHT). The isopropanol/acetone solution may be prepared, for example, by mixing 1 part by volume of isopropanol and 4 parts by volume of acetone.

[0035] The polymer nanoparticles may be functionalized via one or more mechanisms, including functionalization by a specifically designed initiator; functionalization by a specifically designed terminating agent; functionalization by copolymerization of a functionalized comonomer when generating the surface layer and/or the core; or functionalization by modification of any unsaturated groups such as vinyl groups in the poly(conjugated diene) surface layer. Exemplary functional groups that may be incorporated into the polymer nano-particles include, but are not limited to, maleimide, hydroxyl, carboxy, formyl, azocarboxy, epoxide, amino, colonids, bromide, and the like, and the mixture thereof.

[0036] In one exemplary embodiment, polymer nanoparticles are made according to the following process. First, a random poly(conjugated diene) block is prepared through the solution polymerization of conjugated diene monomers and mono-vinyl aromatic monomers in a hexane solvent using a butyl-lithium initiator and in the presence of a randomizing agent, oligomeric oxolanyl propanes (OOPs). The conjugated diene monomers may comprise 1,3-butadiene and the mono-aromatic monomers may comprise styrene. Second, a mixture of mono-vinyl aromatic monomers and multiple-vinyl aromatic monomers is then copolymerized with the living poly(conjugated diene) block, optionally using an additional amount of butyl lithium initiator. The mono-vinyl aromatic monomers may comprise styrene and the multiple-vinyl aromatic monomers may comprise divinylbenzene. The reaction is terminated with alcohol and then dried and desolventized. The product is a star-shaped polymer nanoparticle with a crosslinked core.

[0037] The polymer nanoparticle may take the shape of nano-spheres. The mean diameter of the spheres may be within the range of from about 5nm to about 200nm, or from about 5nm to about 100nm, or from about 10nm to about 80nm, or from about 15nm to about 60nm.

[0038] The molecular weight (M_n , M_w or M_p) of the poly(conjugated diene) block may be controlled within the range of from about 1,000 to about 1,000,000, within the range of from about 1,000 to about 100,000, or within the range of from about 1,000 to about 80,000.

[0039] In a variety of exemplary embodiments, the molecular weight (M_n , M_w or M_p) of the polymer nano-particle may be controlled within the range of from about 100,000 to about 1,000,000,000, or from about 1,000,000 to about 100,000,000. The polydispersity (the ratio of the weight average molecular weight to the number average molecular weight) of the polymer nano-particle may be controlled within the range of from about 1.01 to about 1.3, within the range of from about 1.01 to about 1.2, or within the range of from about 1.01 to about 1.1.

[0040] The nano-particles can be produced in two polymerization steps, rather than three steps, i.e., mono-vinyl aromatic monomers and multiple-vinyl aromatic monomers, as a mixture, are polymerized in one step or simultaneously, rather than mono-vinyl aromatic monomers are polymerized first, and then multiple-vinyl aromatic monomers are copolymerized or summoned for crosslinking. This simpler process results in a higher yield of particles than in the three-step process (80-98% vs. 40-85%). The process can efficiently yield a high conversion of monomers to high molecular weight nanoparticles (typically > 90% yield of nanoparticles).

[0041] Unlike particles made only from vinyl aromatic monomers, the particles of the invention have a vulcanizable surface layer such as a sulfur curable surface layer. The vulcanizable surface layer is a sulfur or peroxide curable surface layer. Examples of suitable sulfur vulcanizing agents include "rubber maker's" soluble sulfur; elemental sulfur (free sulfur); sulfur donating vulcanizing agents such as organosilane polysulfides, amine disulfides, polymeric polysulfides or sulfur olefin adducts; and insoluble polymeric sulfur.

[0042] The nanoparticles have a core that is sufficiently crosslinked such that the T_g of the nanoparticle core may broadly range from about 150°C to about 600°C, from about 200°C to about 400°C, or from about 250°C to about 300°C. Glass transition temperature may be determined, for example, by a differential scanning calorimeter at a heating rate of 10°C per minute.

[0043] The nano-particles are compounded into a rubber composition, such as a tire rubber tread composition. Rubber compositions may be prepared by mixing a rubber and the nano-particles with a reinforcing filler comprising silica, or a carbon black, or a mixture of the two, optionally a processing aid, optionally a coupling agent, optionally a cure agent, other desirable or acceptable tire tread components, and an effective amount of sulfur to achieve a satisfactory cure of the composition.

[0044] Exemplary rubbers include conjugated diene polymers, copolymers or terpolymers of conjugated diene monomers and monovinyl aromatic monomers. These can be utilized as 100 parts of the rubber in the tread stock compound i.e. make up the entire rubber component of the compound, or they can be blended with any conventionally employed treadstock rubber which includes natural rubber, synthetic rubber and blends thereof. Such rubbers are well known to those skilled in the art and include synthetic polyisoprene rubber, styrene-butadiene rubber (SBR), styrene-isoprene rubber, styrene-isoprene-butadiene rubber, butadiene-isoprene rubber, polybutadiene, butyl rubber, neoprene, acrylonitrile-butadiene rubber (NBR), silicone rubber, the fluoroelastomers, ethylene acrylic rubber, ethylene-propylene rubber, ethylene-propylene terpolymer (EPDM), ethylene vinyl acetate copolymer, epichlorohydrin rubber, chlorinated polyethylene-propylene rubbers, chlorosulfonated polyethylene rubber, hydrogenated nitrile rubber, tetrafluoroethylene-propylene rubber, and the like.

[0045] Examples of reinforcing silica fillers which can be used in the vulcanizable elastomeric composition include wet silica (hydrated silicic acid), dry silica (anhydrous silicic acid), calcium silicate, and the like. Other suitable fillers include aluminum silicate, magnesium silicate, and the like. Among these, precipitated amorphous wet-process, hydrated silicas are preferred. Silica can be employed in the amount of about one to about 100 parts per hundred parts of the elastomer (phr), preferably in an amount of about 5 to 80 phr and, more preferably, in an amount of about 30 to about 80 phrs. The useful upper range is limited by the high viscosity imparted by fillers of this type. Some of the commercially available silica which can be used include, but are not limited to, HiSil® 190, HiSil® 210, HiSil® 215, HiSil® 233, HiSil® 243, and the like, produced by PPG Industries (Pittsburgh, Pa.). A

number of useful commercial grades of different silicas are also available from DeGussa Corporation (e.g., VN2, VN3), Rhone Poulenc (e.g., Zeosil® 1165MP0, and J. M. Huber Corporation).

[0046] The rubber can be compounded with all forms of carbon black, optionally additionally with silica. The carbon black can be present in amounts ranging from about one to about 100 phr. The carbon black can include any of the commonly available, commercially-produced carbon blacks, but those having a surface area of at least 20 m²/g and, or preferably, at least 35 m²/g up to 200 m²/g or higher are preferred. Among useful carbon blacks are furnace black, channel blacks, and lamp blacks. A mixture of two or more of the above blacks can be used in preparing the carbon black products of the invention. Typical suitable carbon blacks are N-110, N-220, N-339, N-330, N-352, N-550, N-660, as designated by ASTM D-1765-82a.

[0047] Certain additional fillers can be utilized including mineral fillers, such as clay, talc, aluminum hydrate, aluminum hydroxide and mica. The foregoing additional fillers are optional and can be utilized in the amount of about 0.5 phr to about 40 phr.

[0048] Numerous coupling agent and compatibilizing agent are known for use in combining silica and rubber. Among the silica-based coupling and compatibilizing agents include silane coupling agents containing polysulfide components, or structures such as, for example, trialkoxyorganosilane polysulfides, containing from about 2 to about 8 sulfur atoms in a polysulfide bridge such as, for example, bis-(3-triethoxysilylpropyl) tetrasulfide (Si69), bis-(3-triethoxysilylpropyl) disulfide (Si75), and those alkyl alkoxysilanes of the such as octyltriethoxy silane, and hexyltrimethoxy silane.

[0049] Processing oils can be added to the vulcanizable elastomeric composition. Processing oils may be utilized in the amount of 0 phr to about 70 phr. The processing oil may be added to the composition by itself, or may be added in the form of an oil extended elastomer. Exemplary processing oils include aromatic, naphthenic, and low PCA oils. Suitable low PCA oils include those having a polycyclic aromatic content of less than 3 percent by weight as determined by the IP346 method. Procedures for the IP346 method may be found in Standard

Methods for Analysis & Testing of Petroleum and Related Products and British Standard 2000 Parts, 2003, 62nd edition, published by the Institute of Petroleum, United Kingdom. Suitable low PCA oils include mild extraction solvates (MES), treated distillate aromatic extracts (TDAE), and heavy naphthenics. Suitable MES oils are available commercially as Catenex SNR from Shell, Prorex 15 and Flexon 683 from ExxonMobil, VivaTec 200 from BP, Plaxolene MS from TotalFinaElf, Tudalen 4160/4225 from Dahleke, MES-H from Repsol, MES from Z8, and Olio MES S201 from Agip. Suitable TDAE oils are available as Tyrex 20 from ExxonMobil, VivaTec 500, VivaTec 180 and Enerthene 1849 from BP, and Extensoil 1996 from Repsol. Suitable heavy naphthenic oils are available as Shellflex 794, Ergon Black Oil, Ergon H2000, Cross C2000, Cross C2400, and San Joaquin 2000L.

[0050] It is readily understood by those having skill in the art that the rubber composition can be compounded by methods generally known in the rubber compounding art, such as mixing the rubber(s) with various commonly used additive materials such as, for example, curing agents, activators, retarders and accelerators processing additives, such as oils, resins, including tackifying resins, plasticizers, pigments, additional fillers, fatty acid, zinc oxide, waxes, antioxidants, anti-ozonants, and peptizing agents. As known to those skilled in the art, depending on the intended use of the rubber composition, the additives mentioned above are selected and commonly used in the conventional amounts.

[0051] In one embodiment, the nano-particles are added to a tire tread that comprises at least one rubber. Exemplary rubbers include conjugated diene polymers, copolymers or terpolymers of conjugated diene monomers and mono-vinyl aromatic monomers. These can be utilized as 100 parts of the rubber in the tread stock compound i.e. make up the entire rubber component of the compound, or they can be blended with any conventionally employed treadstock rubber which includes natural rubber, synthetic rubber and blends thereof. Such rubbers are well known to those skilled in the art and include synthetic polyisoprene rubber, styrene-butadiene rubber (SBR), styrene-isoprene rubber, styrene-isoprene-butadiene rubber, butadiene-isoprene rubber, polybutadiene, butyl rubber, neoprene, acrylonitrile-butadiene rubber (NBR), silicone rubber, the fluoroelastomers, ethylene acrylic

rubber, ethylene-propylene rubber, ethylene-propylene terpolymer (EPDM), ethylene vinyl acetate copolymer, epichlorohydrin rubber, chlorinated polyethylene-propylene rubbers, chlorosulfonated polyethylene rubber, hydrogenated nitrile rubber, tetrafluoroethylene-propylene rubber, and the like.

[0052] In another embodiment, a tire tread comprises at least two rubbers, each of which is comprised of at least one conjugated diene monomer unit and at least one mono-vinyl aromatic monomer unit. Exemplary conjugated diene monomers include, but are not limited to, 1,3-butadiene, isoprene (2-methyl-1,3-butadiene), *cis*- and *trans*-piperylene (1,3-pentadiene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, *cis*- and *trans*-1,3-hexadiene, *cis*- and *trans*-2-methyl-1,3-pentadiene, *cis*- and *trans*-3-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, and the like, and the mixture thereof. In preferred embodiments, isoprene or 1,3-butadiene or mixture thereof is used as the conjugated diene monomer. Exemplary mono-vinyl aromatic units include, but are not limited to styrene, ethylvinylbenzene, α -methyl-styrene, 1-vinyl naphthalene, 2-vinyl naphthalene, vinyl toluene, methoxystyrene, t-butoxystyrene, and the like; as well as alkyl, cycloalkyl, aryl, alkaryl, and aralkyl derivatives thereof, in which the total number of carbon atoms in the monomer is generally not greater than about 18; and mixtures thereof.

[0053] The nano-particles can be used in place of the (mono-vinyl aromatic-conjugated diene) copolymer rubber that has a mono-vinyl aromatic content that most closely matches the mono-vinyl aromatic content of the surface layer of the nano-particles. The mono-vinyl aromatic content of the surface layer of the nano-particles can be between about 50 percent and about 150 percent, or between about 75 percent and about 125 percent, or between about 90 percent and 110 percent that of the mono-vinyl aromatic content of one of the (alkenylbenzene-conjugated diene) copolymers. This allows for the incorporation of the nano-particles into the rubber without significantly impacting the overall mono-vinyl aromatic content of the rubber matrix.

[0054] The nano-particles can be added to a rubber composition at a level of less than about 50 phr, less than about 30 phr, or less than about 20 phr.

[0055] The core of the nano-particle acts as a filler dispersed in the rubber. The filler effect is attributed to the relative hardness of the core in comparison to the rubber matrix.

EXAMPLES

[0056] Three rubber stocks were prepared using the formulations shown in Table 1. Stocks 2 and 3 had 7 phr and 14 phr, respectively, of nano-particles of the present invention incorporated in place of the styrene-butadiene rubber with the most similar styrene content. The properties of the nano-particles used are shown in Table 2. Figure 1 shows a DSC analysis of the nano-particles. Figure 1 indicates that the surface layer of the nano-particles had a T_g of -37° C while the T_g of the core was undetectable, meaning the T_g of the core was above 200° C.

[0057] Viscoelastic properties of the three cured rubber stocks are shown in Table 3 wherein the results were obtained from temperature sweep experiments. Temperature sweep experiments were conducted using a spectrometer at a frequency of 50 Hz and a 0.2% strain for the temperature ranging from -50° C to -5° C, and a 1% strain for the temperature ranging from -5° C to 60° C.

[0058] Rubber compounds 2 and 3 which contained the nano-particles exhibited an 11% and 25% increase in E' at 30° C, respectively, which is indicative of an improvement in cornering and steering response. Despite the substantial increase in the dynamic storage modulus, stocks 2 and 3 showed only a 2% and 10% increase in tan δ at 60° C, respectively, which is indicative of slightly higher rolling resistance. Thus, the nano-particles allow for a substantial improvement in the dynamic storage modulus without significantly impacting the hysteresis of the compound.

Table 1

Compound Formulations			
Component (phr)	Comparative Stock 1	Stock 2	Stock 3
Solution SBR ¹	67	67	67
Emulsion SBR ²	33	26	19
Nanoparticles ³		7	14
Carbon Black (N134)	49.5	49.5	49.5
Silica	30	30	30
Bis-3-triethoxysilylpropyl disulfide	2.4	2.4	2.4
Hydrocarbon Resin	8	8	8
Oil	25.13	25.13	25.13
Wax	2	2	2
AO	1.8	1.8	1.8
Stearic Acid	1	1	1
Processing Aid	0.8	0.8	0.8
Zinc Oxide	2.5	2.5	2.5
Sulfur	1.85	1.85	1.85
N-cyclohexyl-2-benzothiazole sulfenamide	1.8	1.8	1.8
Diphenylguanidine	0.8	0.8	0.8
2,2-Dibenzothiazole disulfide	0.4	0.4	0.4

¹Solution SBR (40.5% styrene)²Emulsion SBR (23.5% styrene)³Nanoparticle properties shown in Table 2

Table 2

Nano-Particle Properties	
Surface Layer Tg (°C)	-37
Core % of Total Molecular Weight	31.3
Core Composition	86% styrene / 14% divinylbenzene
Surface Layer Composition	styrene-butadiene
Surface Layer Molecular Weight	119,000
% Styrene in Surface Layer	25%

Table 3

	Comparative Stock 1	Stock 2	Stock 3
E* @ -20° C (Mpa)	997	1182	1277
E' @ 0° C (Mpa)	48.6	51.9	58.3
E' @ 30° C (Mpa)	19.5	21.6	24.4
Tan δ @ 0° C	0.749	0.733	0.725
Tan δ @ 30° C	0.436	0.442	0.454
Tan δ @ 60° C	0.314	0.320	0.345

[0059] An exemplary embodiment has been described. Obviously, modifications and alterations will occur to others upon reading and understanding the preceding detailed description. It is intended that the exemplary embodiment be construed as including all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.

Claims:

1. A composition comprising:

- (a) at least two (mono-vinyl aromatic-conjugated diene) copolymer rubbers, and
- (b) a polymeric nano-particle comprising a poly(mono-vinyl aromatic) core and a poly(mono-vinyl aromatic-conjugated diene) surface layer;

wherein the core of the polymeric nano-particle has a glass transition temperature (T_g) of between about 150° C and about 600° C, and

the poly(mono-vinyl aromatic-conjugated diene) surface layer of the polymeric nano-particle comprises a mono-vinyl aromatic content that is between about 50 percent and about 150 percent that of the mono-vinyl content of one of the (mono-vinyl aromatic-conjugated diene) copolymer rubbers.

2. The composition of claim 1, wherein the surface layer of the polymeric nano-particle comprises a mono-vinyl aromatic content that is between about 75 percent and 125 percent that of the mono-vinyl aromatic content of one of the (mono-vinyl aromatic-conjugated diene) copolymer rubbers.

3. The composition of claim 1, wherein the surface layer of the polymeric nano-particle comprises a mono-vinyl aromatic content that is between about 90 percent and 110 percent that of the mono-vinyl aromatic content of one of the (mono-vinyl aromatic-conjugated diene) copolymer rubbers.

4. The composition of claim 1, wherein said poly(mono-vinyl aromatic) core

comprises polystyrene, and said poly(mono-vinyl aromatic -conjugated diene) surface layer comprises a poly(styrene-butadiene).

5. The composition of claim 1, wherein the polymeric nano-particle has a mean average diameter between about 5 and 200 nanometers.

6. A tire comprising a tread, wherein said tread comprises:

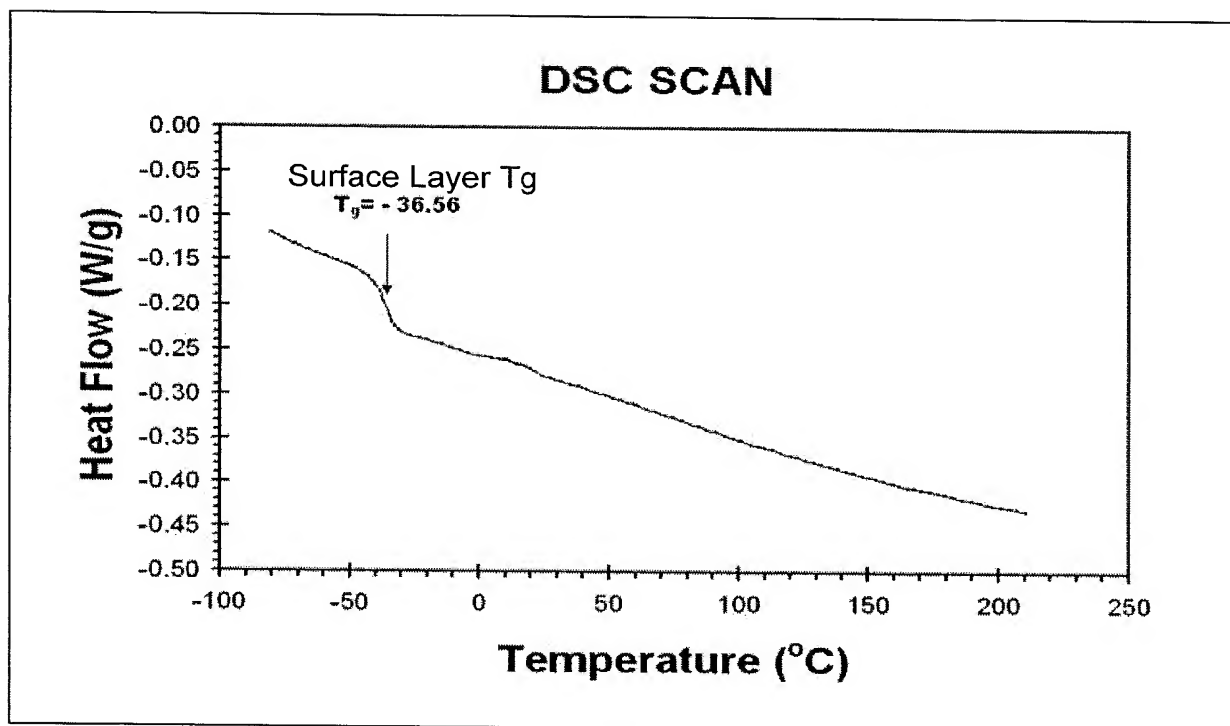
- (a) at least two (mono-vinyl aromatic-conjugated diene) copolymer rubbers, and
- (b) a polymeric nano-particle comprising a poly(mono-vinyl aromatic) core and a poly(mono-vinyl aromatic-conjugated diene) surface layer,

wherein the core of the polymeric nano-particle has a glass transition temperature (T_g) of between about 150° C and about 600° C, and

the poly(mono-vinyl aromatic-conjugated diene) surface layer of the polymeric nano-particle comprises a mono-vinyl aromatic content that is between about 50 percent and about 150 percent that of the mono-vinyl content of one of the (mono-vinyl aromatic-conjugated diene) copolymer rubbers.

7. The tire of claim 6, wherein said rubber comprises at least two (mono-vinyl aromatic-conjugated diene) copolymer rubbers, and the surface layer of the polymeric nano-particle comprises a mono-vinyl aromatic content that is between about 50 percent and about 150 percent that of the mono-vinyl aromatic content of one of the (mono-vinyl aromatic-conjugated diene) copolymer rubbers.

8. The tire of claim 6, wherein the surface layer of the polymeric nano-particle comprises a mono-vinyl aromatic content that is between about 75 percent and 125 percent that of the mono-vinyl aromatic content of one of the (mono-vinyl aromatic-conjugated diene) copolymer rubbers.
9. The tire of claim 6, wherein said at least two (mono-vinyl aromatic-conjugated diene) copolymer rubbers are each styrene-butadiene copolymers.
10. The tire of claim 6, wherein the wherein said poly(mono-vinyl aromatic) core comprises polystyrene, and said poly(mono-vinyl aromatic -conjugated diene) surface layer comprises a poly(styrene-butadiene).
11. The tire of claim 6, wherein the core of the polymeric nano-particle has a Tg of between about 200° C and about 400° C.

**Figure 1**

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2007/087869

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08L9/06 C08L51/06 C08L53/00 B60C1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/085040 A (BRIDGESTONE CORP [JP]; WANG XIAORONG [CN]; LIN CHENCHY JEFFREY [US]; H) 16 October 2003 (2003-10-16)	1-11
Y	abstract; claims; examples 29,30,39-42 page 23, line 6 - line 8	1-11
Y	US 2004/127603 A1 (LEAN JOHN THOMAS [US] ET AL) 1 July 2004 (2004-07-01) cited in the application abstract; claims; tables 1-3 paragraphs [0002], [0009], [0015], [0016], [0020]	1-11
P,A	US 2007/196653 A1 (HALL JAMES E [US] ET AL) 23 August 2007 (2007-08-23) abstract; claims; examples	1-11

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

16 April 2008.

Date of mailing of the international search report

27/05/2008

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Mettler, Rolf-Martin

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2007/087869

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 03085040	A	16-10-2003	AU 2002367717 A1	20-10-2003
			CN 1639203 A	13-07-2005
			EP 1432740 A2	30-06-2004
			JP 2005537341 T	08-12-2005
			US 2005192408 A1	01-09-2005
			US 2006084722 A1	20-04-2006
			US 2003149185 A1	07-08-2003
<hr/>				
US 2004127603	A1	01-07-2004	NONE	
<hr/>				
US 2007196653	A1	23-08-2007	NONE	
<hr/>				